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SHELF LIFE DETERMINATION OF EPOXY PREPREGS
AND FILM ADHESIVES

B. G. Parker

Bendix Corporation
Kansas City, Missouri

January 1979

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B. G. Parker, Project Leader

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SHELF LIFE DETERMINATION OF EPOXY PREPREGS AND FILM ADHESIVES

BDX-613-2033 (Rev.), Final Report, Published January 1979

Prepared by B. G. Parker

Kinetic data describing the cure of a Kevlar/epoxy prepreg and an epoxy film adhesive were determined by the use of Differential Scanning Calorimetry. For the Kevlar/epoxy prepreg, a correlation was found between the heat of reaction and percent resin flow; a similar correlation was found between the heat of reaction and lap-shear strength for the film adhesive. An equation was derived for the determination of the "B" stage time required to yield an epoxy prepreg possessing the desired flow properties. The effects of storage temperature on the shelf-life of both the prepreg and film adhesive were determined.

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CONTENTS

Section	Page
SUMMARY.	5
DISCUSSION	6
SCOPE AND PURPOSE.	6
PRIOR WORK	6
ACTIVITY	7
<u>Derivation of Kinetic Data From DSC Scans.</u>	7
<u>Shelf-Life Aging</u>	8
<u>Film Adhesive.</u>	15
ACCOMPLISHMENTS.	16
FUTURE WORK.	17
REFERENCES	21
DISTRIBUTION	22

ILLUSTRATIONS

Figure		Page
1	Isothermal DSC Curve for Kevlar/Epoxy Prepreg, Lot 10.	9
2	Typical Dynamic DSC Curve, Using Kevlar/ Epoxy Prepreg, Lot 10.	10
3	Isothermal Reaction Rates for a Kevlar/Epoxy Prepreg, Lot 10.	11
4	Arrhenius Plot of Isothermal DSC Data for a Kevlar/Epoxy Prepreg, Lot 10	12
5	Resin Flow Versus Heat of Reaction for Kevlar/Epoxy Prepreg, Lot 10	14
6	Lap Shear Strength Versus Heat of Reaction for a Film Adhesive.	18
7	Softening Temperature Versus Heat of Reaction for a Film Adhesive	19

TABLES

Number		Page
1	Physical Properties of a Kevlar/Epoxy Prepreg.	13
2	"B" Stage Effects on Kevlar/Epoxy Prepreg . .	15
3	Physical Properties of a Film Adhesive	17
4	Aging Effects on Physical Properties of a Film Adhesive.	17
5	Shelf Life of a Film Adhesive.	20

SUMMARY

Kinetic data (such as reaction order, heat of reaction, activation energy, and frequency factor), which describe the cure of two epoxy resin systems, were determined by the use of Differential Scanning Calorimetry (DSC).

A direct correlation between the heat of reaction and resin flow was found for a Kevlar/epoxy prepreg (Kevlar is a registered trade name of Du Pont Corp.). Use of the same "B" stage conditions for different lots of the Kevlar/epoxy prepreg did not result in material possessing the same resin flow properties. An equation was derived for the determination of the "B" stage time required to yield a material having the desired resin flow properties.

A correlation was also found between the heat of reaction and the lap-shear strength of a film adhesive. DSC analysis does appear to be a viable method for incoming inspection of preform film adhesives which cannot be lap-shear tested.

An equation was also derived for the determination of the shelf-life expected at any storage temperature for both epoxy systems investigated. Use of this equation demonstrated the need for a subambient storage temperature for both materials to slow down aging and to lengthen shelf-life.

DISCUSSION

SCOPE AND PURPOSE

Differential Scanning Calorimetry (DSC) offers a relatively fast method of evaluating the degree of "B" staging of epoxy preregs and film adhesives. In addition, DSC permits determination of kinetic data useful in evaluating the shelf-life stability and the effects various storage conditions have on this property. Because DSC requires a very small sample (10 to 20 mg), it would also provide a method for incoming inspection of preform film adhesives as well as permitting extension of their shelf-life.

The purpose of this project was to compare DSC data with flow test results of a prepreg to evaluate shelf-life stability. In addition, lap shear tests on a film adhesive, were compared with DSC data to determine if a preform film adhesive that cannot be lap shear tested could be tested by a DSC method for lot acceptance.

PRIOR WORK

It has been shown¹ that, by assuming the extent of reaction is proportional to the heat evolved, the Arrhenius equation becomes:

$$\frac{1}{H_T} + \frac{dH}{dt} = A_e - \frac{E_a}{RT} \left(\frac{H}{H_T} \right)^n = \frac{E_a}{RT} \cdot \left(\frac{H_T - H}{H_T} \right)^n \quad (1)$$

or, in the more useful logarithmic form,

$$\ln \frac{dH}{dt} - n \ln \frac{H_r}{H_T} = -\frac{E_a}{RT} + \ln A = \ln k \quad (2)$$

where

H_T = total heat of reaction (cal/g), which is equal to the area under the DSC curve;

H_r = $H_T - H$ = heat of reaction remaining at a given time and temperature which is equal to the partial area remaining;

E_a = Arrhenius activation energy (kcal/mol);

A = Arrhenius equation frequency factor;

n = reaction order;

k = reaction rate;

R = gas constant;

T = temperature (K); and

f (H/H_T) = a function of H_T which is assumed here to be (H_r/H_T)ⁿ.

The ratio Ea/n can be obtained from the equation

$$\frac{E_a}{n} = \frac{RT^2}{H_r \beta} \left(\frac{dH}{dt} \right)_{\max} \quad (3)$$

where dH/dt and T are taken at the maximum point on the DSC curve and β is the heating rate dT/dt.

Using the alternate Freeman-Carroll method of analysis, the activation energy can be obtained by comparing two DSC curves at different heating rates.^{2,3} Assuming the fractions reacted at maximum dH/dt are the same and independent of the heating rate and that the frequency factor A is constant, the following equation can be used.

$$\frac{\Delta \ln(\beta/T)^2}{\Delta 1/T} = \frac{-E_a}{R} \quad (4)$$

ACTIVITY

Derivation of Kinetic Data From DSC Scans

Differential Scanning Calorimetry was performed both in the isothermal and dynamic modes of operation on three lots of Kevlar/epoxy prepreg. Figures 1 and 2 show typical isothermal and dynamic DSC scans of the epoxy-prepreg investigated.

By plotting ln H_r versus time (t) for isothermal DSC runs, the curves shown in Figure 3 were obtained. The fact that the curves were straight lines was a good indication of a first order reaction. The Arrhenius plot shown in Figure 4 was obtained by plotting the slope of the three curves in Figure 3 versus 1/T. The slope of the Arrhenius curve in Figure 4 is equal to Ea/R;

this results in an activation energy of 24.8 kcal/mol. The ratio of E_a/n for lot 10 of the Kevlar/epoxy prepreg was found, by using the data obtained from a dynamic DSC scan, at a heating rate of 2°C/min and Equation 3 to be 23.8 kcal/mol. The E_a as determined by using the DSC data and Equation 4 was 23.12 kcal/mol, hence a reaction order of 1.03. The other epoxy system investigated was a film adhesive and was also found to follow first order kinetics; therefore, in all further calculations it was assumed that the reaction order, n , was equal to one, and activation energies were calculated by the use of Equation 3. The frequency factor, A , was calculated from the equation

$$\ln A = \ln \frac{dH}{dt} \cdot \frac{1}{H_T} - \ln \left(\frac{H_r}{H_T} \right) + \frac{E_a}{RT} \quad (5)$$

as derived from equation 2.

Listed in Table 1 is the kinetic data obtained from triplicate DSC scans of three lots of a Kevlar/epoxy prepreg along with some physical data. Resin solids were measured by extracting a sample with acetone for 4 hours using an extractor and measuring the amount of material remaining in the extraction thimble. The percent resin flow was measured by placing 4 plies of prepreg, each 10.16 by 10.16 cm, between a release film of Kapton (a registered trade name of Du Pont Corp.) in a heated press at 135°C at a pressure of 69 kPa for 10 minutes. The resin which flowed outside the Kevlar cloth was broken off and weighed. The resin flow was measured as the percent of resin which was removed, based on the initial weight of the 4 plies of prepreg. The Bendix material specification for epoxy prepreg specifies a resin flow of 25 to 35 percent and a resin solids content of 45 to 55 percent.

Shelf-Life Aging

It has previously been suggested that the H_T values for epoxy resin prepreps are very useful for measuring shelf life aging and predicting processing characteristics.⁴ By comparing the H_T values of Table 1 with the resin flow data, there does appear to be a correlation.

Further evidence for this correlation was found by "B" staging (partially curing) the epoxy prepreg at 80°C for various time intervals and measuring both the H_T and resin flow of the "B" staged material. The result of this testing is shown in Figure 5. The percent resin flow is directly proportional to the H_T of the prepreg and the current specification for resin flow of 25 to 35 percent would correspond to an H_T of 50.5 to 60 cal/g.

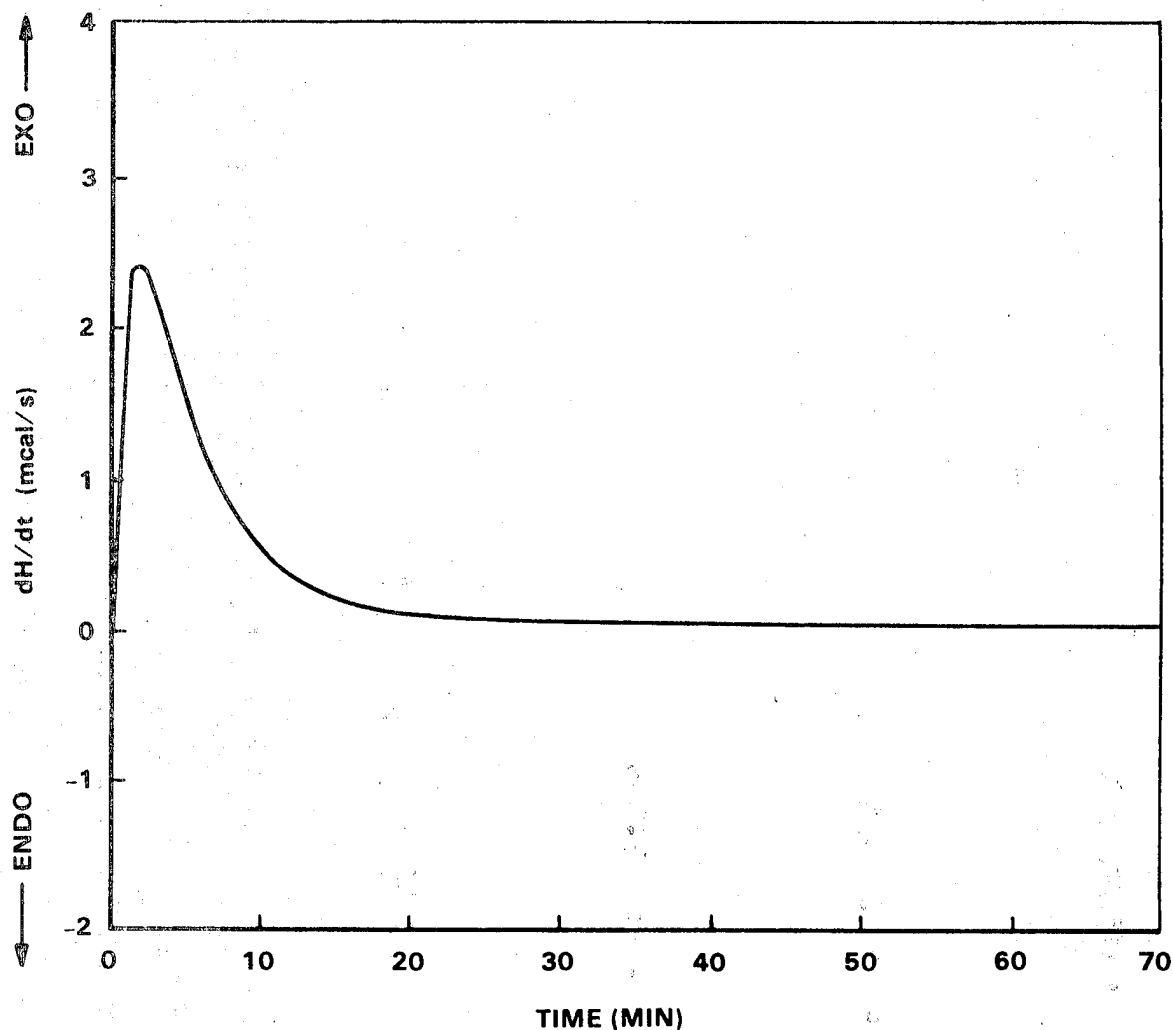


Figure 1. Isothermal DSC Curve for Kevlar/Epoxy Prepreg, Lot 10

While the H_T would appear to be useful as an alternate to the resin flow method for lot acceptance, it alone is not sufficient for predicting the processability of the prepreg. During the processing of the prepreg to yield a part having specific density and dimensional requirements, the prepreg is "B" staged for a specified time and temperature prior to molding. The amount of "B" staging controls the amount of flash which is removed after molding. Too much "B" staging results in less flash, a lower density, and a larger part. Too little "B" staging results in excessive flash, a higher density, and a smaller part.

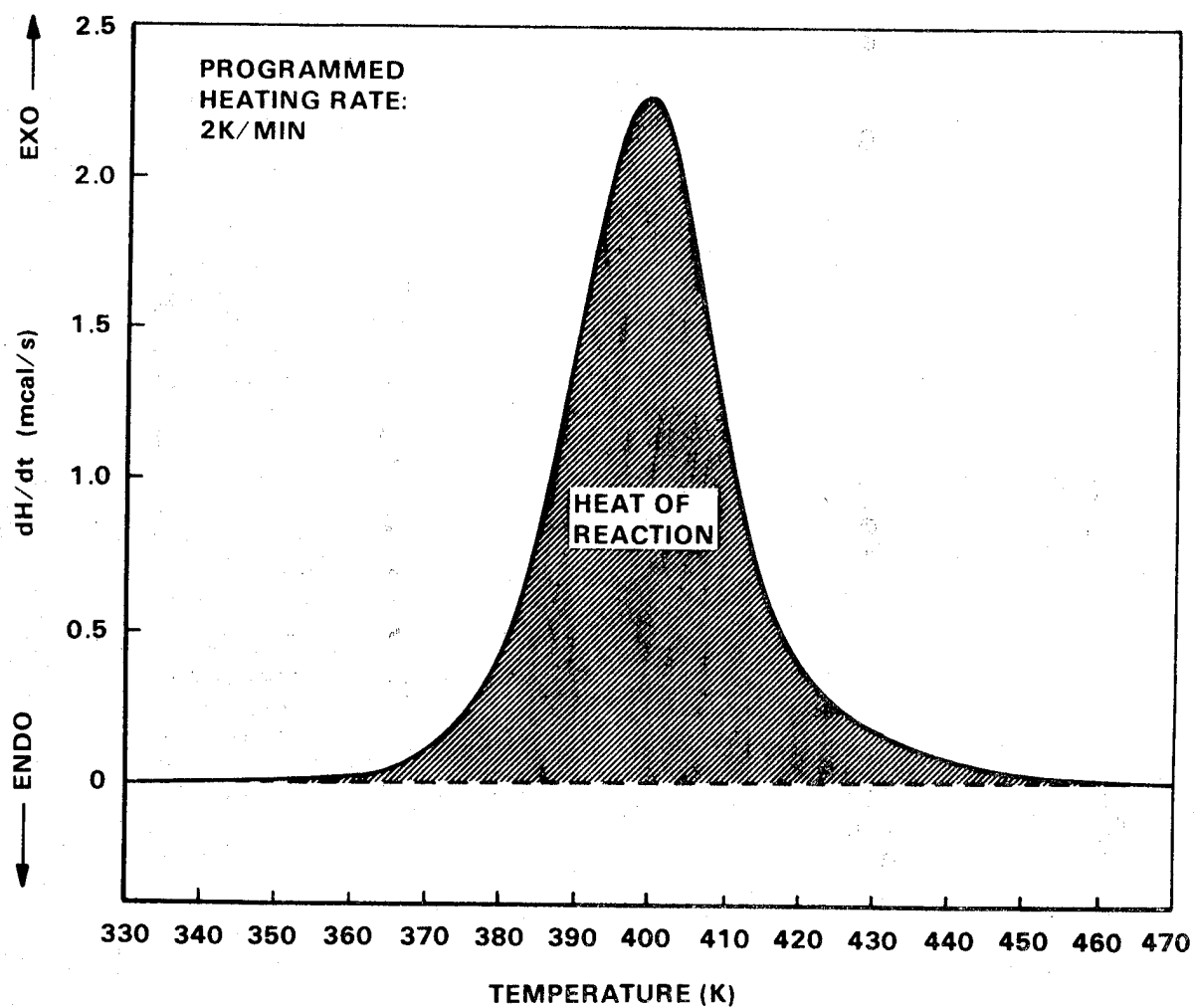


Figure 2. Typical Dynamic DSC Curve, Using Kevlar/Epoxy Prepreg, Lot 10

An equation was derived to predict the effect of "B" staging on the heat of reaction remaining (H_r):

$$H_r = H_T e^{-t[Ae(-E_a/RT)]} \quad (6)$$

where

H_T is the initial total heat of reaction,

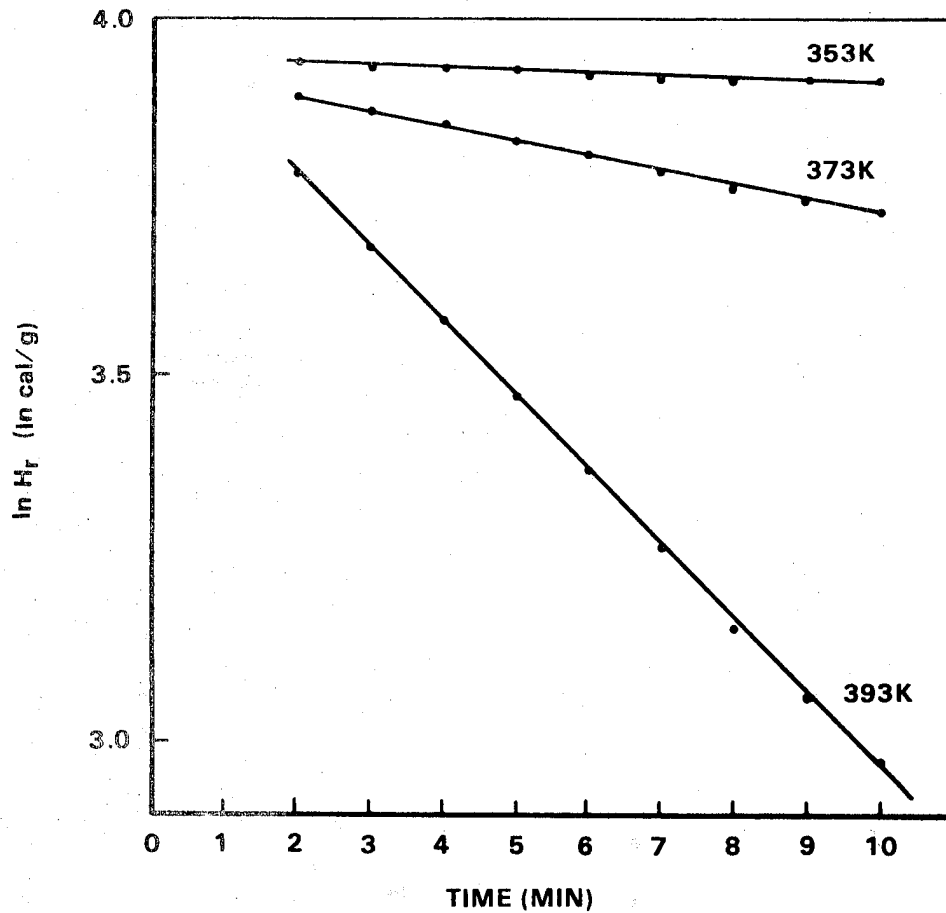


Figure 3. Isothermal Reaction Rates for a Kevlar/Epoxy Prepreg, Lot 10

T is the "B" stage temperature in Kelvins, and

t is the "B" stage time in seconds.

If a specific remaining heat of reaction H_r is desired, the following equation can be used to determine the "B" stage time required.

$$t = \frac{e^{E_a/RT}}{A} \ln \frac{H_T}{H_r} \quad (7)$$

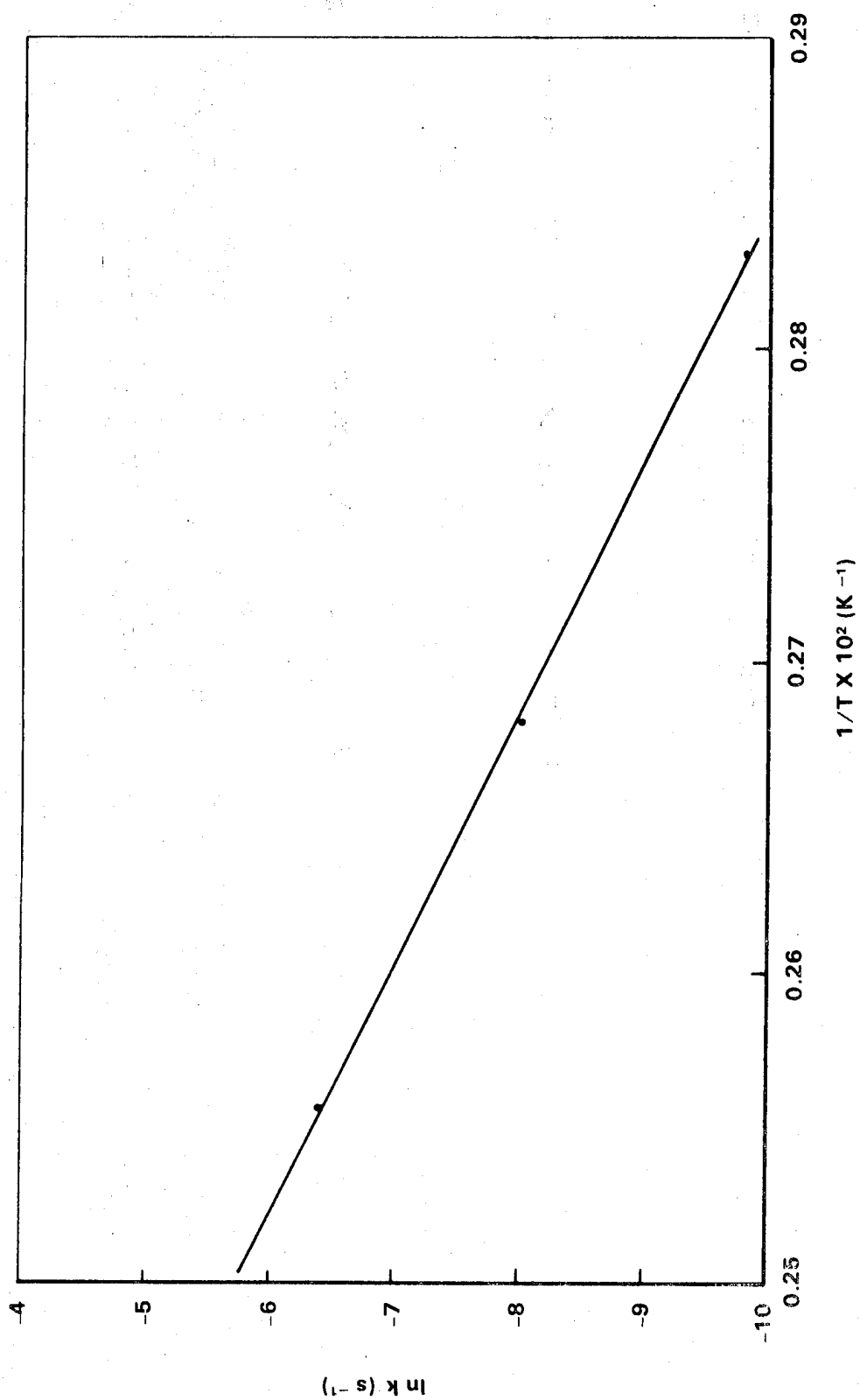


Figure 4. Arrhenius Plot of Isothermal DSC Data for a Kevlar/Epoxy Prepreg, Lot 10

Table 1. Physical Properties of a Kevlar/Epoxy Prepreg

Physical Property	Lot Number		
	10	13	15
Temperature, T (dH/dt) _{max} (K)	401	399	397
Heat of Reaction, H _r (cal/g)	51.1 ±0.6	53.7 ±0.4	48.1 ±1.0
Arrhenius Activation Energy, E _a (kcal/mol)	23.8 ±0.6	22.9 ±0.6	24.6 ±0.6
Arrhenius Equation Frequency Factor, ln A (s ⁻¹)	24.1 ±0.8	23.1 ±0.8	25.5 ±0.9
Resin Flow (Percent)	26.1	28	23
Resin Solids (Percent)	44.3	47.2	49.4

The three lots of Kevlar/epoxy prepreg were subjected to the same amount of "B" staging (one hour at 80°C) and then the H_r was determined by duplicate DSC scans. The result of this testing, along with the predicted H_r value derived by using Equation 6, is shown in Table 2. The predicted H_r shown in Table 2 match the measured H_r fairly closely and demonstrate the usefulness of the DSC data.

It can also be seen from Table 2 that using the same "B" stage conditions for three different lots of prepreg resulted in material having a large difference in resin flow properties. These differences would lead to finished parts having different densities and dimensions. By using Equation 7, it is possible to determine the "B" stage time and temperature required to yield the desired H_r and percent resin flow. This would allow better control of the final part density and size.

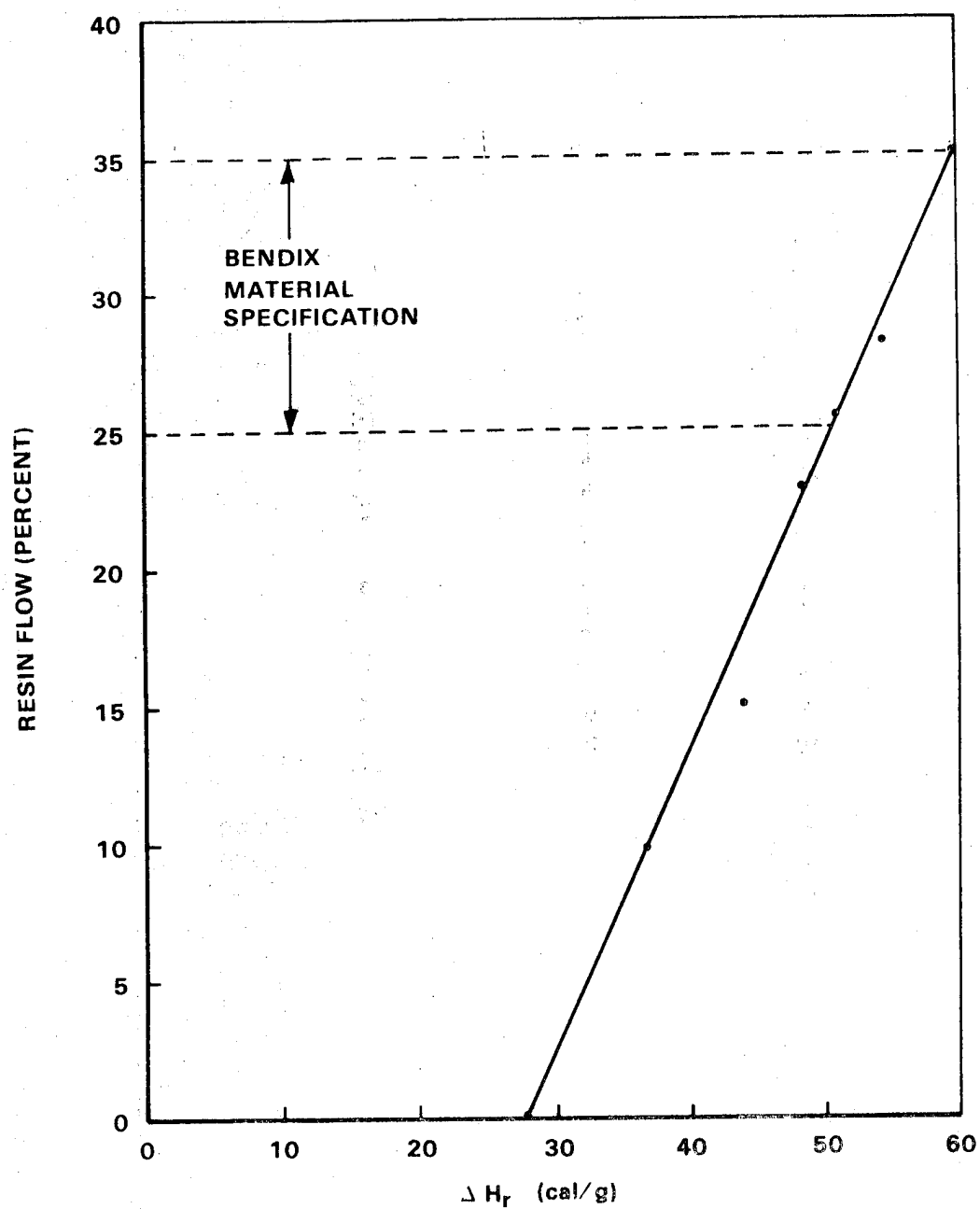


Figure 5. Resin Flow Versus Heat of Reaction for Kevlar/Epoxy Prepreg, Lot 10

Table 2. "B" Stage Effects on Kevlar/Epoxy Prepreg

Physical Property	Lot Number		
	10	13	15
Initial H_T (cal/g)	51.1 \pm 0.6	53.7 \pm 0.4	48.1 \pm 1.0
H_T After "B" Staging (cal/g)	45.1 \pm 2.6	35.1 \pm 2.1	31.9 \pm 1.2
Predicted H_T (cal/g)	42.1	35.8	32.0
Initial Resin Flow (Percent)	26.1	28	23
Resin Flow* After "B" Staging (Percent)	18.8	7.8	4.5

*Predicted flow, obtained from Figure 5.

Equation 7 can also be used for evaluating the shelf-life at various storage temperatures for this or similar epoxy prepregs. If, for example, a heat of reaction of 49 cal/g is chosen as the minimum value required to meet acceptance tests, then, by using Equation 7, the shelf life of lot 10 would be 188 days at 0°C and 4.7 days at 25°C; the shelf life of lot 13 would be 212 days at 0°C and 6.2 days at 25°C. This demonstrates the need for maintaining a subambient storage temperature and avoiding temperature excursions prior to its being used. Shelf life of lot 15 was not calculated, because its heat of reaction initially was below the arbitrary minimum value.

Film Adhesive

Another epoxy material investigated is a film adhesive. DSC analysis showed kinetic properties very similar to the Kevlar/epoxy prepreg. This is not surprising, because both materials are composed of similar epoxy resins and both use dicyandiamide as a cure agent. The film adhesive uses nylon net (roughly 4 percent by weight) as the carrier, instead of Kevlar as used in the Kevlar/epoxy prepreg.

As previously mentioned, the film adhesive was also found to follow first order kinetics. The results of DSC analysis and lap shear testing are shown in Table 3.

To determine the effect of aging on the adhesive properties of this material, Lot 2-28-78 was "B" staged for 4, 8, and 16 hours at 60°C. After "B" staging, the aged material was analyzed by DSC, lap shear tested, and the softening temperature measured by thermomechanical analysis (TMA). Softening temperature (T_s) was determined at a heating rate of 5°C/min and a load weight of 10 g on a penetration probe. The results of these analyses are shown in Table 4.

Again, the predicted heat of reaction remaining after "B" staging matched the actual measured values fairly closely. Also, a correlation was found between the remaining heat of reaction and both lap shear data and the softening temperature. These correlations are further shown in Figures 6 and 7.

The shelf-life of the film adhesive can be evaluated by the method previously described for Kevlar/epoxy prepreg. If a heat of reaction of 49 cal/g is again chosen as the minimum value required to meet acceptance tests, then, by using Equation 7, the shelf-life of the three lots would be as shown in Table 5.

Again, the need for storing the material at a subambient temperature was seen. Any exposure to room temperature during transportation to the plant, within the plant, or delays during processing would greatly shorten the shelf-life of this material.

ACCOMPLISHMENTS

The kinetic data describing the cure of two epoxy systems, the Kevlar/epoxy prepreg and the film adhesive, were determined by the use of DSC.

Correlations were found between the heat of reaction and resin flow for the Kevlar/epoxy prepreg and between the heat of reaction and lap shear strength for the film adhesive. These correlations show that DSC analysis could be a suitable method for incoming inspection of both epoxy systems.

An equation was derived for the determination of the shelf-life, at any storage temperature, for the two epoxy resin systems investigated.

Table 3. Physical Properties of a Film Adhesive

Physical Property	Lot Designation		
	B-1077	DSE	2-28-78
$T (dH/dt)_{\max}$ (K)	392	391	395
H_T (cal/g)	53.2	51.2	50.7
E_a (kcal/mol)	25.6	26.6	25.1
$\ln A$ (s^{-1})	2.0	28.4	26.2
Lap Shear* (MPa)	27.7	21.3	20.5

*Average values for five specimens.

Table 4. Aging Effects on Physical Properties of a Film Adhesive

Aging Time at 60°C	H_T (cal/g)		Lap Shear** (MPa)	T_s (°C)
	Actual	Predicted*		
Initial	50.7		20.5	18
4 hr	46.0	45.2	17.5	35
8 hr	39.6	40.2	12.9	45
16 hr	31.1	31.9	10.9	54

*From Equation 7.

**Average values for five test specimens.

FUTURE WORK

The kinetic data describing the cure of one Kevlar/epoxy prepreg and one film adhesive were determined; however, there are many other epoxy-prepregs and film adhesives in use which could be evaluated in a similar method.

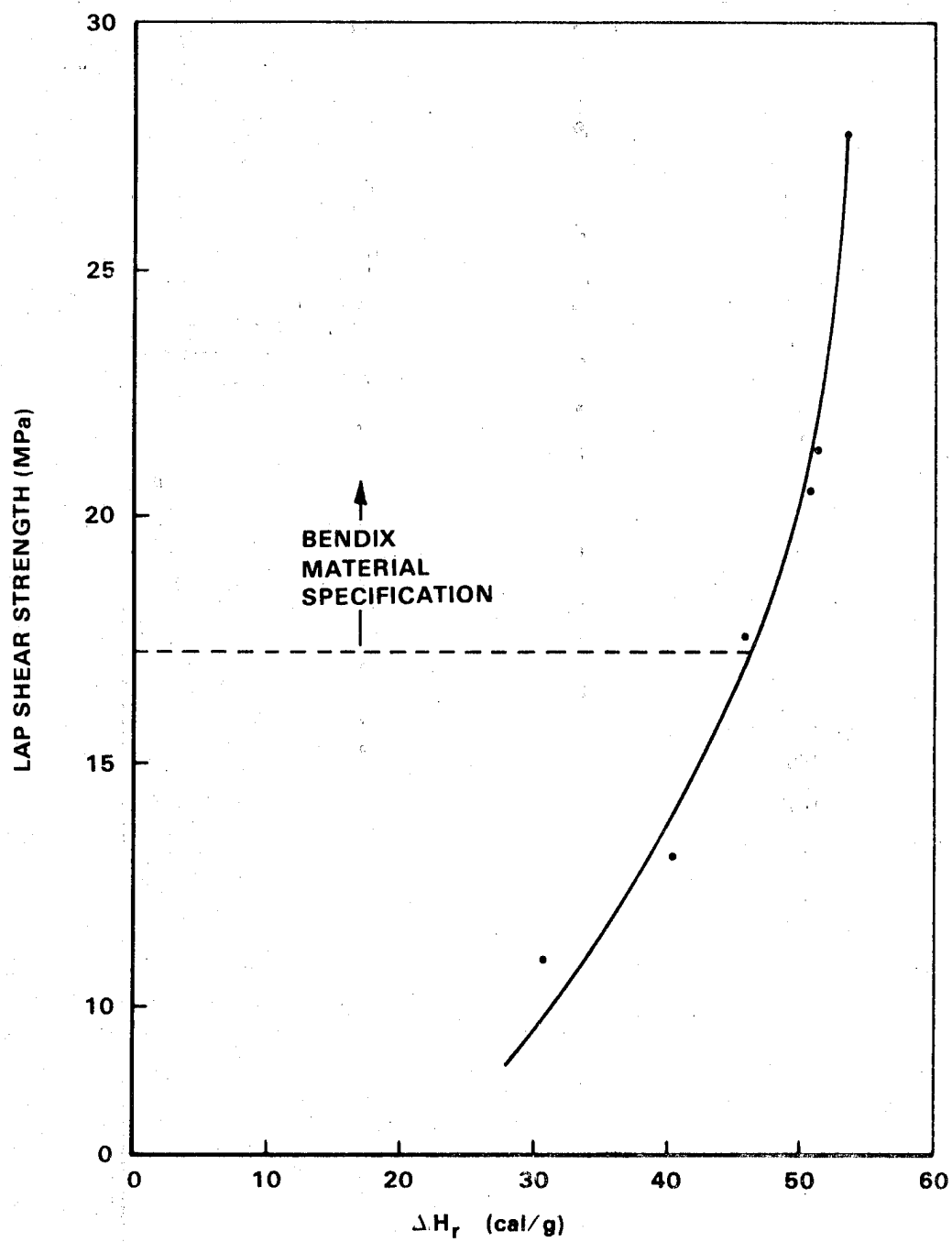


Figure 6. Lap Shear Strength Versus Heat of Reaction for a Film Adhesive

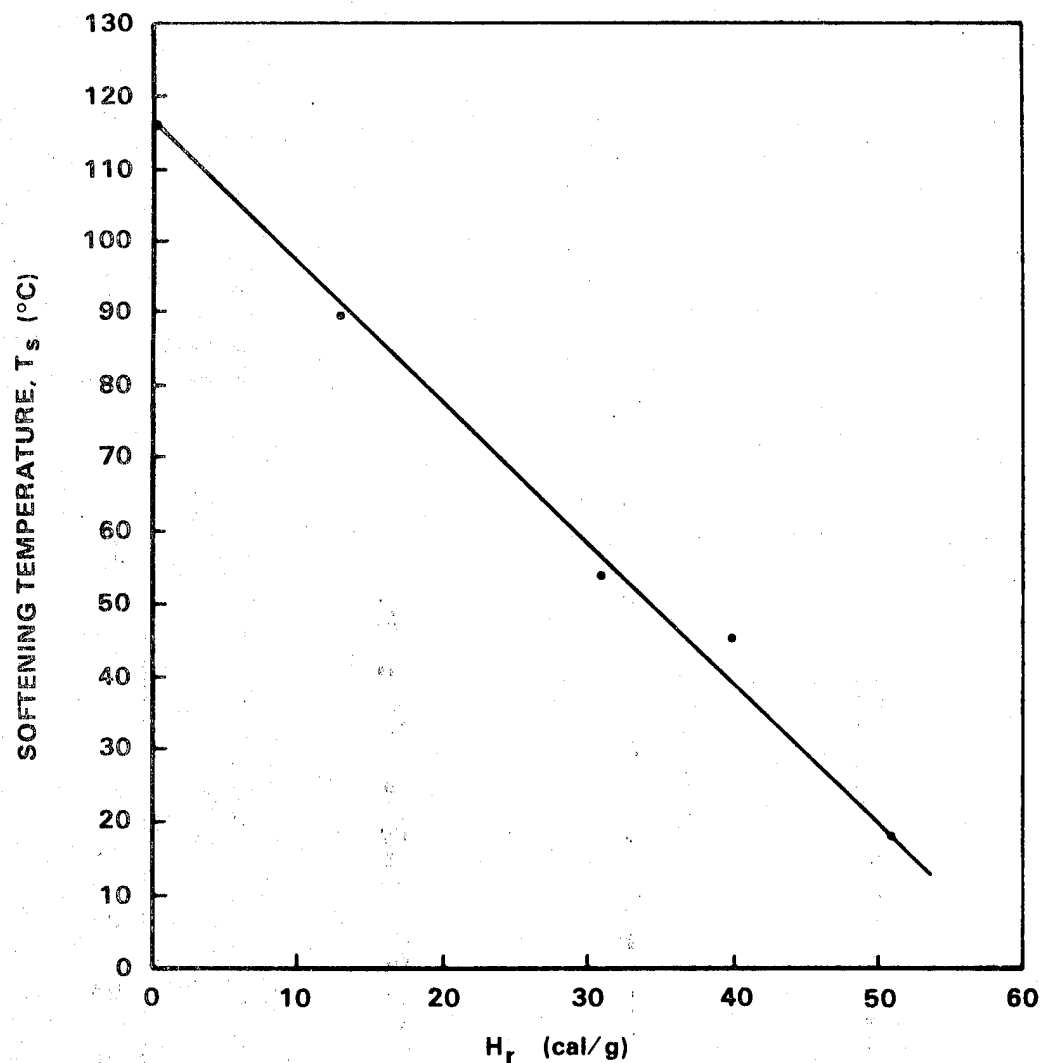


Figure 7. Softening Temperature Versus Heat of Reaction for a Film Adhesive

Once the kinetic data were determined, the shelf-life and the effects of storage temperature could be determined. In addition, the use of such kinetic data could aid in the processing of epoxy-prepregs which require "B" staging prior to use.

Table 5. Shelf Life of a Film Adhesive

Lot Designation	Shelf Life (Days) at Storage Temperature	
	0°C	25°C
B-1077	560	10.7
DSE	466	7.6
2-28-78	206	4.2

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